-- CHROMIC ACID AND ITS DERIVATIVES --

GENERAL INFORMATION

INDUSTRIAL HEALTH ASPECTS

INDUSTRIES AND OCCUPATIONS

SELECTED ABSTRACTS

SELECTED REFERENCES

OHIO DEPARTMENT OF HEALTH. Division of Adult Hygiene
R. H. MARKWITH, M.D.
Director of Health
Columbus, Ohio
1940

This material compiled by the Adult Hygiene Division of the Ohio Department of Health, assisted by the personnel of Work Projects Administration in Ohio, Official Project No. 665-42-3-413.

1940

-- C H R O M I C A C I D A N D I T S D E R I V A T I V E S --

The element chromium was discovered in 1797 by L.N. Vanquelin whose work was later confirmed by M.H. Klaproth. The first description of ulcerations among dichromate workers was made by Glascow in 1827 and reported in 1851.

The recent introduction of chromium plating in industry on a wide scale has resulted in an increase of exposures to chromic acid. However, the incidence of chrome ulcers among electroplaters has been substantially reduced in those plants using proper ventilation facilities on the plating tanks.

It should be emphasized that the derivatives of chromic acid do not include such compounds as chromium sulfate, chrome alum, and chromium chloride. Chromic acid and its derivatives contain hexavalent chromium atoms and are toxic. The trivalent chromium compounds also commonly used in industry are usually considered harmless.

GENERAL INFORMATION

CHEMICAL FORMULA AND SYNONYMS:

(Chromic acid) CrO_3, chromic anhydride, chromium trioxide.

(Sodium dichromate) $Na_2Cr_2O_7$-$2H_2O$, sodium bichromate.

PROPERTIES:

(Chromic acid) Reddish brown crystals. Sp. gr. 2.7; m.p. 196°C. Soluble in water and ether. Powerful oxidizing agent. Will inflame organic materials.

(Sodium dichromate) Red, deliquescent, crystalline fragments. Sp. gr. 2.52 at 13°C.; loses-$2H_2O$ at 100°C.; melts at 320°C.; decomposes at 400°C. Soluble in water.

PREPARATION:

(Chromic acid) Hydrochloric or sulfuric acid is added to a solution of sodium dichromate and the product recovered by crystallization; also electrolytically.

(Sodium dichromate) Chrome iron ore is fused in a reverberatory furnace, with lime and soda in presence of air, followed by extraction with water, and acidification with sulfuric acid. The solution is filtered, concentrated and crystallized.

USES:

(Chromic acid) Chemicals (chromates, oxidizing agent, catalysts); intermediates (oxidizing agent); medicine (astringent and germicide); electric cells; ceramic glazes; colored glass; printing and lithographing inks; tanning; paints; rubber pigments; textile mordant; chromium plating.

(Sodium dichromate) Oxidizing agent; alums; dyes; intermediates; pharmaceuticals; perfumery; chrome pigments; tanning; textiles (mordant, oxidizing agent, waterproofing); electroplating; precious metals refining; engraving copper plates; bleaching oils, fats, waxes and sponges; medicine (antiseptic); glues; refining petroleum products; batteries; pyrotechnics; matches, analytical reagent.

INDUSTRIAL HEALTH ASPECTS

MODES OF ENTRANCE:

Inhalation, ingestion, or by absorption through the broken skin.

SYMPTOMS OF INDUSTRIAL POISONING:

Chromic acid and derivatives exhibit a local caustic action and decidedly toxic properties when taken internally; more pronounced in the case of dichromates. When ingested, compounds of chromium cause a disagreeable taste, headache, vomiting, diarrhea, muscular cramps, collapse, unconsciousness, dilated pupils, and slow respiration. The blood pressure is abnormally low in spite of uremic symptoms. At autopsy, there is found hemorrhages in the stomach, intestine, bronchi, pleura and endocardium, fatty degeneration of the liver, and cloudy swelling of the kidneys.

Vapors cause acute dermatitis, stated to be more common among young persons, females, or those predisposed to diseases of the skin.

Bloomfield and Blum suggest that continuous daily exposures be kept below 1 mg. per cubic meter, attainable by proper transverse ventilation.

(Chromic acid) Has a corrosive action on mucous membranes with frequent perforation of the nasal septum and inflammation of the skin with eczematous eruptions and "chrome holes", pit-like ulcers, painful, difficult and slow healing, frequently on the hands. Irritation of the conjunctiva and of the respiratory passages with rare inflammation of small areas in the lungs also occurs. Systemic poisoning (except from accidental ingestion) is not of frequent occurrence in industry. A death from general sepsis, following chronic suppuration of chrome lesions has been reported.

(Sodium dichromate) See chromic acid. Alkaline chromates are decidedly toxic if ingested. They cause a local irritant action (or eczema, as dermatitis) and may also cause ulcer formation, lesions of the respiratory mucous membranes and of the conjunctiva, and perforation of the nasal septum.

INDUSTRIES AND OCCUPATIONS

INDUSTRIES: Ohio Industries using chromic acid and its derivatives as indicated in the Ohio Industrial Hygiene Survey are listed as follows:

Aircraft
Asphalt and roofing materials
Blast furnaces
Brass factories
Car and railroad shops
Chemicals
Clock and watch factories
Dyestuffs, ink
Electric fixtures
Electrical machinery
Electroplating
Explosives, ammunitions and fireworks
Foundries
Glass factories
Match factories
Metal furniture
Other chemicals
Other manufacturing plants
Other metals
Other textiles, etc.
Paint and varnish factories
Patent medicine, drugs
Petroleum refineries
Soap factories
Storage batteries
Woolen and worsted

OCCUPATIONS: Occupations in Ohio where contact with chromic acid and its derivatives was indicated are listed as follows:

Anadizing operators (aircraft)
Apprentices (foundries)
Blueprint men (foundries; storage batteries; brass factories; electrical machinery)
Buffers (foundries; other metals; etc.)
Chemists (dyestuffs, ink)
Chief engineers (petroleum refineries)
Cleaners (brass factories; foundries)
Detailers (storage batteries)
Dippers (brass factories; foundries)
Draftsmen (foundries)
Dryers (brass factories; woolen and worsted)
Dye vat hands (woolen and worsted)
Electroplaters (foundries; storage batteries; blast furnaces; brass factories; chemicals; electrical machinery; electroplating; clock and watch factories; electric fixtures; metal furniture; other metals; other manufacturing plants)
Enamelers (foundries)
Engineers (car and railroad shops)
Explosive makers (explosives, ammunitions, and fireworks)
Foremen (brass factories; electroplating; foundries; other manufacturing plants; other textiles)
Forge press operators (foundries)
Furnace attendants (chemicals)
Furnace room laborers (glass factories)
General superintendents (patent medicine; drugs)
Heaters (foundries)
Hot trimmers (foundries)
Laborers (chemicals; glass factories; other textiles)

Ladelers (glass factories)
Managers (electroplating)
Mill operators (paint and varnish factories)
Mixers (paint and varnish factories; laundries; chemicals; match factories; other chemicals; other manufacturing plants)
Mold cleaners (glass factories)
Molders (other manufacturing plants)
Open hearth men (foundries)
Operators (dyestuffs, ink; soap factories; patent medicine, drugs)
Packers (glass factories)
Painters (foundries)
Paint mixers (asphalt and roofing materials)
Picklers (foundries; blast furnaces; electrical machinery)
Polishers (electroplating; foundries; glass factories; other metals, etc.)
Rinsers (brass factories)
Rough grinders (foundries)
Shipping clerks (glass factories)
Stock clerks (foundries)
Technicians (patent medicine, drugs)
Tracers (foundries)
Weighers (other manufacturing plants)

Occupations which offer contact with chromic acid and its derivatives but not listed in the Ohio Survey are:*

Acetylene workers
Battery (dry) makers
Bleachers
Chrome workers
Frosters (glass and pottery)
Match factory workers
Photo-engravers
Photographic workers
Steel (chrome) workers
Tannery workers

*Dublin, L.I., and Vane, R.J.: Occupation Hazards and Diagnostic Signs. U.S. Department of Labor, Bureau of Labor Statistics, Bulletin 582:35, 1933.

SELECTED ABSTRACTS

THE TOXICOLOGY OF CHROMIUM.

Keiji Akatsuka, M.D., M.P.H., D.P.H., and Lawrence T. Fairhall, S.M., Ph.D. From the Department of Physiology, Harvard School of Public Health, Boston.

Abstracted from J. of Ind. Hygiene, vol. 16, no. 1, pp. 1-18 (text section) Jan. 1934.

SUMMARY

Chromic salts such as chromic carbonate and chromic phosphate are not poisonous to cats whether introduced through the digestive tract or the respiratory system.

Relatively gross amounts of chromium as chromic carbonate dust may be inhaled, and large quantities of chromic salts may be ingested without causing any illness or producing any tissue damage. Chromium, when present in the form of chromic salt, is apparently very inert and presents a striking contrast to the properties of the derivatives of chromic acid in this respect. In view of the enormously increased industrial utilization of chromium, a sharp distinction should be made between chromic salts, which are relatively inert and harmless, and the derivatives of chromic acid, which certainly exhibit toxic properties.

CHROME PLATING AND ITS OCCUPATIONAL RISKS.

Roels. Rev. du travail, 1931, vol. 32, pp. 116-128.

Abstracted in J. of Ind. Hygiene, vol. 13, no. 7, pp. 163-164 (abstract section) Sept. 1931.

The advantages obtained by chrome plating are stated as follows: exceptional hardness, and resistance to heat and to chemical agencies. The method followed in plating by electric baths is described briefly and clearly. Iron and steel articles are first coated with copper and nickel. In every case, if a polished surface is desired, the article to be plated must first be polished, as the coating of chrome is too hard to be polished after deposition. If the bath is worked at a temperature of from 20° to 25°C., a mat surface results; if it is worked from 35° to 38°C., a polished surface is obtained. When the bath is in action, oxygen and hydrogen are given off, and steps must be taken to prevent them from exploding. At the same time bubbles of gas carry up droplets of chromic acid from the bath. If these are inhaled, they attack the mucous membrane of the nose and injure the nasal septum, thus causing perforation. This process, however, gives rise to no trouble or inconvenience to the worker, who often is quite unaware that his nasal septum is perforated. If the chromic acid solution falls upon abraded skin of the hands, it attacks it by setting up painful and indolent ulcers or chrome holes, which differ in no way from chrome holes occurring in other occupations. These occupational troubles can be entirely prevented (1) by a suitably arranged exhaust draft placed over the electrolytic bath to draw away all gases as they are evolved, and (2) by the use of rubber gloves to keep any splashes from the bath off the skin of the attendant.--E.L.C.

PERFORATION OF THE NASAL SEPTUM IN CHROMIUM WORKERS. REPORT OF EIGHTEEN CASES.

F.W. Dixon. Jour. Am. Med. Assn., Sept. 14, 1929, vol. 93, pp. 837-838.

Abstracted in J. of Ind. Hygiene, vol. 12, no. 4, p. 73 (abstract section) April 1930.

Dixon reports eighteen cases of perforation of the cartilaginous portion of the nasal septum in men engaged in chromium plating.

Chromium plating is accomplished by immersing the object to be plated in an electrolytic vat containing, among other elements, chromic acid. In this electrodeposition, oxygen is evolved on the insoluble anode and considerable hydrogen on the cathode. These gases, rising, tend to carry into the surrounding air a fine mist or spray of chromic acid. This spray, on being inhaled, deposits the chromic acid particles inside the nose on the mucous membrane.

Chromic acid affects persons exposed by causing lesions of the skin and irritations of the nose. It affects the abraded skin, causing deep ulceration. If affects the nose in causing an inflammation of the mucous membrane with ulceration of the nasal septum, which may later lead to perforation. This final process is painless and is neither disabling nor disfiguring, but does cause inconvenience through crusting.

In plating rooms where proper ventilation of the tanks and rooms is employed, irritation is not encountered, but natural room ventilation is not sufficient.

In those already afflicted, the free application of white petrolatum to the septum caused all unpleasant symptoms to disappear. The use of mercurochrome and medicated petrolatum was not helpful. When irritations are noted, daily check-up by the nurse, coupled with regular inspection by the medical attendant, is advisable. Employees must be warned not to pick at their noses, since the chromic acid on their fingers increases the exposure. The wearing of masks and gloves, while helpful, is difficult of enforcement.--K.R.D.

NASAL CHANGES IN CHROMIUM WORKERS.

G. Mancioli. Rass. med. indust., vol. 9, pp. 258-271 (1938).

Abstracted in J. of Ind. Hygiene, vol. 21, no. 7, pp. 168-169 (abstract section) Sept. 1939.

In the past year, while visiting factories as a government specialist, the author has seen 300 cases of chromium poisoning. They were much more frequently encountered in small, poorly ventilated shops where the work was not isolated. Since the only untoward sensation is burning in the nose, the workers are seldom aware of ulceration, and frequently exaggerate the trouble by putting their dirty fingers into their noses.

Prevention by good ventilation of dipping tanks is recommended as is the liberal use of boric vaseline or salicylic ointment in the nose.

Proper masks and rubber gloves should be worn by those exposed.--A.J. Collis (Bull. Hyg., condensed).

PROTECTION OF WORKERS IN CHROMATING PLANTS.

Forster. Zentralbl. f. Gewerbehyg., May 1926, N.S. vol. 3, pp. 124-125.

Abstracted in J. of Ind. Hygiene, vol. 9, no. 2, p. 31 (abstract section) Feb. 1927.

The unusually advantageous properties of chromium-extreme hardness, heat stability, complete resistance to chemical influence-have caused it to be employed in very many industries. In the metal industry, it is used in the manufacture of dental and surgical instruments, cutlery, and automobiles. The extended use of chromium demands consideration for the protection of the workmen.

Above the galvanic baths in which the chromating takes place, a brown mist may be seen hanging over the surface of the water. This mist is composed of fine particles of chromium which are thrown off by the galvanic process and are poisonous. It is self-evident that an exhaust appliance is indispensable, and that it should be placed directly over the water in the bath, and kept constantly in operation.

Chromium causes inflammation of the mucous membrane of the nose, which soon develops into an ulcer and may lead to perforation of the nasal septum. Ulcers appear also on the lips, arms, hands, and feet.

Workers should be instructed regarding the dangers, and should be held to strictest cleanliness. It is also important that they have suitable working clothing, as well as dressing, wash, and lunch rooms.

The galvanic baths should be operated by some adult and well-informed person. Medical examinations should be made of each worker when first employed, and each month thereafter. Special attention should be given to the skin and to the nasal septum.--A.W.N.

OCCUPATIONAL DISEASES AMONG WORKERS IN THE CHROMATES.

J.A.M.A. (Belgian letter), vol. 109, p. 1922 (Dec. 4, 1937).

Abstracted in J. of Ind. Hygiene, vol. 20, no. 4, p. 83 (abstract section) April 1938.

Workers exposed to alkaline chromates and bichromates display several types of dermatitis; ulceration, upper respiratory tract troubles such as rhinitis and perforation of the nasal septum; also conjunctivitis, ulcers of the mouth, tonsils and pharynx. Generalized intoxication is rare. The lesions are caused by the dust and vapors. Enclosing the apparatus and hygienic measures for the workers, as well as careful selection of employees are suggested as preventive measures.--Helen Lawson.

TREATMENT OF CHROME ULCERS BY ULTRAVIOLET RADIATION.

A. Dewirtz. Works of Institute for Experimental Medicine, Sverdlovsk, vol. 61 (1935).

Abstracted in J. of Ind. Hygiene, vol. 18, no. 6, p. 83 (abstract section) June 1936.

The excellent results of treatment by ultraviolet radiation of chrome ulcers is described in this article. In all cases the ulcers that were previously unsuccessfully treated by various unguents were cured definitely by ultraviolet rays in a short time. In the chromate plant in Sverdlovsk by the use of Dach's lamp, early forms of the disease were cured.--O. Gandin.

FATAL POISONING FROM CHROMIC ACID.

Goertz. Arbeitsschutz, pp. 183-184 (1939).

Abstracted in J. of Ind. Hygiene, vol. 21, no. 8, p. 192 (abstract section) Oct. 1939.

Chromic acid is used to clean scales and rust from boilers. In performing such work, two workers got splashed in the face with the acid. One died of nephritis 2 weeks later. Another worker is reported to have died from absorbing the poisoning through a small wound.--L. Teleky.

CHROMIUM.

Safe Practice Sheet No. 3, Nat. Safety News, Oct. 1925, p. 63.

Abstracted in J. of Ind. Hygiene, vol. 8, no. 3, p. 53 (abstract section) March 1926.

This series of Safe Practice Sheets, prepared by the Industrial Poisons Committee, Chemical Section, National Safety Council, presents summaries of the present practice in the prevention of industrial poisoning.--M.C.S.

SELECTED REFERENCES

Belgian Letter: Occupational Diseases Among Workers in the Chromates. Jour. Am. Med. Assn., vol. 109, p. 1922, Dec. 4, 1937.

Blair, J.: Chrome Ulcers. Report of Twelve Cases. Jour. Am. Med. Assn., vol. 90, pp. 1927-1928, June 16, 1928.

Blair, J.: Health Hazards in Chromium Plating. Ohio State Med. Jour., vol. 27, p. 142, Feb. 1931.

Bloomfield and Blum: Health Hazards in Chromium Plating. Public Health Reports, Sept. 7, 1928, pp. 2330-2347.

Chrome Plating and Anodic Oxidation: Reprinted from Form 1891, April 29, 1930, Home Office, London.

Foreign Letter (Japan): Poisoning from Chromium. Jour. Am. Med. Assn., vol. 89, p. 2055, Dec. 10, 1927.

Gerbis: The Protection of the Nasal Septum from Corrosive Action of Inhaled Chromates. Zentralbl. f. Gewerbehyg., N.S. vol. 1, pp. 10-11, July 1924.

Gorodetskii, G.A., and Makhover, S.L.: Determination of Small Quantities of Chromium in the Air of Industrial Plants. Hig. Truda 15, no. 1, pp. 84-85, 1937; Chimie and industrie, vol. 38, p. 889.

Hamilton, A.: Industrial Toxicology. Harper and Bros., Publishers, New York, 1934, pp. 17-19.

Industrial Poisons Committee, Chemical Section, National Safety Council: Chromium. Safe Practice Sheet No. 3, p. 63, Oct. 1925.

Industry Rep., Retail Credit Co.: Chromium Plating, vol. 4, pp. 1-6, July 1929.

Joules, H.: Asthma from Sensitization to Chromium. Lancet., pp. 182-183, July 23, 1932.

Kober, G., and Hayhurst, E.: Industrial Health. P. Blakiston's Son and Co., Publishers, Philadelphia, 1924, pp. 588, 651, and 847.

Labat, J.A.: Toxicology and Hygiene of Chromium. Bull. trav. soc. pharm. Bordeaux, vol. 76, pp. 191-201, 1938.

Lapin, N.P., Warganow, W.F., Druskin, S.L., Worochobin, I.G., and Sapolsky, W.W.: Industrial Hygiene Measures in Chromium Plating. Gigiena Truda i tekhnika bezopasnosti., no. 5, pp. 51-55, 1934.

McNally, W.: Toxicology. Industrial Medicine, Publishers, Chicago, 1937, pp. 126-129.

Mauro, V.: Cachexia and Hematological Alterations in Experimental Chromium Poisoning. Rass. Med. all. al Lavoro Ind., vol. 6, pp. 435-440, 1936.

Mikhal'chishin, G.T.: Drop Method for an Approximate Determination of Chromium. Univ. etat Kiev, Bull. sci., Rec. chim. no. 3, pp. 85-89, 1937.

Occupation and Health. International Labour Office, Geneva, 1930, pp. 437-448.

St. Galloro: Experimental Investigation on Occupational Chromium Poisoning in the Electro-Chromium Plating Industry. Folia med., vol. 24, pp. 1256-1265, 1938.

Shaverdova, E.I.: Protector Liquid in Electrolytic Chromium Plating. Gigiena truda i tek. bezopasnosti., no. 1, pp. 89-91, 1937.

van der Walt, C.F.J., and van der Merwe, A.J.: Colorimetric Determination of Chromium in Plant Ash, Soil, Water, and Rocks. Analyst., vol. 63, pp. 809-811, 1938.

Verkhovskaia, P.I.: Use of Protector Liquids in Chromium Plating. Gigiena truda i tek. bezopasnosti., no. 2, pp. 33-36, 1937.